



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C08B 31/00, D21H 17/29</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 95/18157</b> <b>(43) International Publication Date:</b> 6 July 1995 (06.07.95)
<b>(21) International Application Number:</b> PCT/FI94/00576 <b>(22) International Filing Date:</b> 21 December 1994 (21.12.94) <b>(30) Priority Data:</b> 935883, 27 December 1993 (27.12.93) FI <b>(71) Applicant (for all designated States except US):</b> RAISIO CHEMICALS OY [FI/FI]; FIN-21200 Raisio (FI). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> VIHervaara, Tapio [FI/FI]; Rakuunatie 59 A 6, FIN-20720 Turku (FI). PAAKKANEN, Anna [FI/FI]; Kaitoväylä 32 A 14, FIN- 90570 Oulu (FI). KÄKI, Jouko [FI/FI]; Keskitalonkatu 28, FIN-20300 Turku (FI). <b>(74) Agent:</b> OY JALO ANT-WUORINEN AB; Iso Roobertinkatu 4-6 A, FIN-00120 Helsinki (FI).		<b>(81) Designated States:</b> CA, CN, HU, JP, RU, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>In English translation (filed in Finnish).</i>
<b>(54) Title:</b> METHOD FOR PRODUCING OF CATIONIC STARCH  <b>(57) Abstract</b>  The present invention relates to a method of producing cationic starch derivatives in water solution form, in which method the starch structure is split prior to the cationizing step. The solids of the reaction mixture during the cationizing reaction is maintained over 50 %.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

## METHOD FOR PRODUCING OF CATIONIC STARCH

Starch is a raw material commonly used in paper manufacture. The principal role of starch is to improve the strength of paper. Starch can also be used as an adhesive in surface sizing and as a binder in coating formulations in place of a more expensive latex binder.

However, starch both in native unmodified form or modified by oxidization alone bonds weakly to the fiber, whereby the unbonded starch or the starch redissolved during the repulping of broke elevates the chemical and biological oxygen demand of circulating waters, and eventually, of waste water in a paper mill.

The bonding of starch to cellulosic fiber can be improved by adding cationic groups to the primary portion of starch, that is, by cationizing the starch. Cationized starch bonds better to the fiber by virtue of the negative charge, or anionic character, of the cellulosic fiber. By using cationized starches, the addition rate of starch in paper manufacture can be raised substantially without increasing the amount of soluble starch wasted in circulating water, that is, without increasing the chemical and biological oxygen demand of circulating and waste waters.

Several methods have been developed for the cationization of starches. The cationizing chemical can be selected from a group comprising both tertiary and quaternary reagents that are capable of reacting with the OH groups of starch. The cationic character of the reagent results from the nitrogen atom of the reagent. If the nitrogen bonds three substituents, the reagent is called tertiary, while a reagent having four substituents bonded to the nitrogen is called quaternary. Today, a majority of cationic starches is modified with a quaternary reagent such as 2,3-epoxypropylene trimethylammonium chloride or

3-chloro-2-hydroxypropylene trimethylammonium chloride. Quaternary cationizing chemicals are characterized in that they can retain their cationic charge also in so-called neutral paper manufacture performed within the pH range of 6.5 - 8.5.

Of the practicable methods, the most commonly used is the so-called wet method. In this method, starch is slurried in water to form an aqueous suspension with a consistency of approx. 40 %, the cationizing chemical is added and pH is adjusted to within pH 11 - 12. At these conditions and a temperature of approx. 40 - 45 °C, starch will be cationized in a reaction completed in approx. 12 - 16 hours. The starch slurry is usually neutralized at the end of the reaction with a mineral acid such as hydrochloric acid or sulfuric acid, after which the starch can be either filtered and dried prior to shipping to a customer, or alternatively, shipped as such in slurry form. The essential of the method is that the starch stays throughout the process in slurry form, that is, retaining the granular structure of the starch during the entire cationizing step. A limit to the foregoing method is set by the solubility of starch which increases rapidly if the degree of substitution exceeds 0.05. With the increasing solubility of the starch, the mixing of the slurry becomes more difficult and finally impossible due to partial or complete gelation of the starch. Even a slight increase of solubility makes filtration of the starch difficult, finally stopping it altogether.

Also such cationizing methods have been developed in which water as the suspending medium has been replaced by organic solvents, typically alcohols such as ethanol. Then, the degree of substitution can be elevated substantially without causing any significant dissolution of the starch in the suspending medium, that is, the organic solvent. Using ethanol as the suspending medium, the de-

gree of substitution can be easily increased to a range of 0.5 - 1.0. However, the use of organic solvents is not desirable due to occupational health reasons. Moreover, the use of inflammable liquids requires substantial investments in the safety of an industrial plant.

Methods requiring no suspending medium at all have also been developed. In the art of starch making, these are called dry cationization methods. According to such a method, the cationizing chemical essentially consisting of 2,3-epoxypropylene trimethylammonium chloride is blended with a mixture of pulverized starch and a basic catalyst such as NaOH or  $\text{Ca}(\text{OH})_2$ . By agitating the dry mixture with a screw mixer or equivalent agitator, possibly using anticaking agents as additives, sufficient homogeneity is attained. A problem of the method is therein that the purification of the end product is usually impossible. In this method, all chemicals added to the cationization process remain in the modified, pulverized starch, and still worse, a portion of dry-cationized starch becomes cold-soluble during the reaction due to the cationization and temperature applied, thus causing a difficulty in the handling of the cationized starch and particularly the slurring and cooking of the cationic starch at paper mills. However, dry-cationization can achieve a higher degree of cationization than the conventional slurry cationization, that is, the wet cationization.

Further, methods have been developed in which cationization is carried out in an aqueous solution. Here, starch is allowed to gelatinize under the effect of a base and temperature thus dissolving the starch in an aqueous medium, whereby essentially homogeneous reaction conditions are established (as compared with the heterogeneous systems described above). A difficulty herein is formed by the high viscosity of the dissolved cationic

starch. Then, in order to achieve effective utilization of the starch in paper manufacture, that is, in a sufficiently high solids content, the straight-chain portion of starch must first be broken into shorter molecular chains. Conventionally, the chain-shortening methods used include acid hydrolysis or hypochlorite oxidation, for instance.

Both acid hydrolysis and hypochlorite oxidation produce a great amount of soluble, short-chain oligosaccharides which deteriorate the bonding qualities of cationic starch. Hypochlorite oxidation, in particular, produces an abundant number of carboxylic groups in the starch, whereby the quaternary groups of the cationic starch form an internal salt with the acid groups, which lowers the total cationic charge of the starch.

The cationization methods of starch known in the art from patent publications or other sources are divided in accordance with the foregoing into the following categories:

1. Slurry cationization
  - cationization in a water suspension, whereby the solids may be maximally 43 %.
2. Dry cationization
  - the solids may be very high, up to 80 %, while the starch stays in pulverized form throughout the reaction.
3. Solvent cationization
  - water as the reaction medium is replaced by an organic solvent.

Contrary to these conventional methods, the method according to the invention is characterized in that the

starch structure is split prior to the cationizing step and that the solids of the reacting mixture during the cationizing reaction is maintained over than 50 %, advantageously over 55 %. The starch may be, as indicated in the examples below, peroxide treated, while the spirit of the invention obviously does not exclude other possibilities such as oxidizers in particular. These shortening methods of starch chain length are well known in the art.

As is well known, the cationizing reaction requires a basic catalyst, which can be selected from a large group of bases, not only using sodium hydroxide as described in the examples. This detail is not essential to the spirit of the invention.

The cationizing chemical is advantageously 2,3-epoxypropylene trimethyl ammonium chloride which is well known in the art and is only mentioned herein as a reference characterizing the end product.

Essential to the method according to the invention is thus, that the cationizing step is carried out in an aqueous solution in which the solids during the cationizing reaction is maintained over 50 %, advantageously over 55 %.

#### **Example 1**

##### **Hydrogen peroxide oxidation of starch**

Native potato starch was slurried in water by adding 1250 g of starch (solids 80 %) in 1250 g of water, whereby starch slurry of 40 % solids was obtained. The reaction mixture was adjusted to pH 7.5 using dilute sodium hydroxide solution. After thorough mixing, 50 % hydrogen peroxide was added to the slurry. After the completion of the reaction, the slurry was adjusted to pH 6.5 with di-

lute hydrochloric acid. The reaction was repeated with different amounts of hydrogen peroxide in order to determine the effect of the peroxide. The viscosity of the starch determined after the completion of the reaction is listed in Table 1 below.

	H <sub>2</sub> O <sub>2</sub> (% of starch amount)	Viscosity 5 % (at 60 °C)	Sample #
10	0.00	1600	0
	0.02	430	1
	0.06	210	2
	0.08	135	3
15	0.10	105	4
	0.15	62	5
	0.20	31	6
	0.30	22	7

Each test lot was filtered through a paper filter and the proportion of soluble sugars, or oligosaccharides, was computed from the solids of the filtrate. In all cases the amount of such sugars was less than 1 % (while the corresponding amount by hypochlorite oxidization and acid hydrolysis was in the order of 5 - 10 %).

### Example 2

A sample of lot #2 was taken as 40 % slurry from the test series products of the above example and cationized in the formulation described below using 80 % Raisacat 65 (2,3-epoxypropylene trimethylammonium chloride) with 71 % activity.

	Weight	Solids
35 Starch slurry sample #2	2140 g	856 g
Raisacat 65	1130 g	904 g
50 % NaOH	50 g	25 g
40 Total	3320 g	1785 g

The solids content of the reaction mixture was 53.8 %.



The temperature of the reaction mixture was elevated to about 60 °C. The mixture, which changes from a slurry into a solution within approximately 1 h after the caustic addition, was agitated in a reactor equipped with an anchor agitator for 6 h at approx. 60 °C and subsequently neutralized with approx. 50 kg of approx. 30 % hydrochloric acid. Using conventional analytic methods, the degree of substitution in the product was determined as 0.72. The product was diluted to a 20-% aqueous solution for exact determination of viscosity. The viscosity of the product was 2120 cP at 20 °C.

### Example 3

A sample of lot #7 was taken from the test series products of Example 1 and dried to 80 % moisture content. The starch was slurried into a mixture of Raisacat 65 and water, and the caustic was added to achieve the formulation given in the table below. The other steps of this example were performed according to Example 2.

	Weight	Solids
Starch slurry sample #7	1070 g	856 g
Raisacat 65	1130 g	904 g
50 % NaOH	50 g	25 g
Water	550 g	
Total	2800 g	1785 g

The solids content of the reaction mixture was 63.8 %.

The degree of substitution in the product was determined as 0.75. Diluted to 30 %, the viscosity of the product was 880 cP at 20 °C.

**Claims:**

1. A method of producing cationic starch derivatives in water solution form, **characterized** in that the starch structure is split prior to the cationizing step and that the solids of the reacting mixture during the cationizing reaction is maintained over 50 %, advantageously over 55 %.
2. A method as defined in claim 1, **characterized** in that starch is added to the reaction mixture in pulverized or slurry form prior to the cationizing step.
3. A method as defined in claim 1 or 2, **characterized** in that the splitting of starch is performed with the aid of an oxidizer prior to the cationizing step.
4. A method as defined in any of foregoing claims 1-3, **characterized** in that the amount of the cationizing chemical is 40 - 160 %, most advantageously 80 - 120 %, of the amount of starch.
5. A method as defined in any of foregoing claims 1-4, **characterized** in that the cationizing chemical used is 2,3-epoxypropylene trimethyl ammonium chloride.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 94/00576

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
IPC6: C08B 31/00, D21H 17/29 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols)		
IPC6: C08B, D21H		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
SE,DK,FI,NO classes as above		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
CHEMICAL ABSTRACTS		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Chemical Abstracts, Volume 120, No 24, 13 June 1994 (13.06.94), (Columbus, Ohio, USA), THE ABSTRACT No 301471, FI, B, 90679, (Vihervaara, Tapio et al) 30 November 1993 (30.11.93), the whole abstract  ---	1,5
A	US, A, 4146515 (PETER D. BUIKEMA ET AL), 27 March 1979 (27.03.79), the whole document  -----	1-5
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
2 March 1995		05 -04- 1995
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86		Authorized officer  Agneta Österman Wallin Telephone No. +46 8 782 25 00

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

09/02/95

International application No.

PCT/FI 94/00576

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FI-B- 90679	30/11/93	NONE	
US-A- 4146515	27/03/79	NONE	